Dynamic Solvent Effects in Adiabatic Electron-Transfer Reactions: Role of Translational Modes

B. Bagchi,* A. Chandra,
Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore 560 012, India

and G. R. Fleming
Department of Chemistry and James Franck Institute, University of Chicago, Chicago, Illinois 60637

(Received: December 4, 1989; In Final Form: March 13, 1990)

A molecular theory of the dynamic solvent effects on an outer-sphere adiabatic electron transfer reaction is presented. The theory properly includes the role of the microscopic correlations present in a dense dipolar solvent in the dynamics of an electron-transfer reaction. The theory predicts that the translational modes of the solvent, hitherto neglected in most discussions on electron-transfer reactions, can significantly enhance the rate of an adiabatic electron-transfer reaction.

Introduction
The possible role of polar solvent dynamics in influencing the rate of an electron-transfer reaction has been a subject of several theoretical studies in recent years.1-4 While the majority of the theoretical predictions are yet to be confirmed, recent experimental results seem to indicate a definite role of polar solvent dynamics in determining the rate of an outer-sphere electron-transfer reaction.5 Several computer simulation studies6-7 have also addressed the problem of solvent involvement in the dynamics of electron-transfer reactions in dipolar solvents.

In this Letter we present a molecular theory of dynamic solvent effects on an outer-sphere adiabatic electron-transfer reaction. This theory extends the earlier theoretical studies1-4 in several directions. First, microscopic descriptions of the structure and the dynamics of the solvent are included self-consistently. Most of the earlier studies were based on a continuum model description of the solvent. For dynamic solvent effects, such continuum model description can be seriously flawed because the continuum model includes only the long wavelength relaxation processes whereas in electron transfer, the intermediate wavelengths are quite important. Second, we include, for the first time, the effects of the translational modes of the solvent in the dynamics of electron transfer. We show that these translational modes can have a significant effect on the dynamics of electron transfer; especially, they can significantly enhance the rate over that given by the rotational modes alone.

Models
We shall consider two different models of electron-transfer reactions in this work. In the first model, the reaction involves an isolated redox couple
\[ \text{Ox} + e = \text{Red} \] (1)
This model has been studied recently by McManis and Weaver, who used the dynamic mean-spherical approximation (DMSA) of Wolynes to find the dynamic solvent effects on the adiabatic barrier-crossing frequency. As pointed out by McManis and Weaver, this reaction can be thought of as an electrochemical exchange process, with the reactant located sufficiently far from the metal surface. The net free energy driving force for this reaction is zero, so that the free energy of activation, \( \Delta G^\# \), is the "intrinsic" outer shell (i.e., solvent) part of the barrier energy. In this case, the reaction coordinate is the solvation energy of the reaction system in the state of Wolynes to find the dynamic solvent effects on an adiabatic electron-transfer reaction. We shall consider only the adiabatic limit where the reaction coordinate time correlation function \( \Delta G^\#(t) \) is defined by the expression recently provided by Hynes. Thus, the problem of calculating the rate constant now reduces to the calculation of the reaction coordinate time correlation function, \( \Delta G^\#(t) \). We next present microscopic calculations of \( \Delta G^\#(t) \) for both the models considered here.

In the first model, the reaction coordinate is the solvation energy of an ion in a dipolar liquid, and in the second model it is that of a dipole. The reaction coordinate time correlation function is given by
\[ \Delta G^\#(t) = \left[ \int dk E_0^\#(k) \delta P_L(-k) \delta P_L(k,t) \right] \times \left[ \int dk E_0^\#(k) \delta P_L(-k) \delta P_L(k) \right] \] (6)
where \( E_0^\#(k) \) is the Fourier transform of the bare electric field of an ion (for model I) or of a dipole (for model II). The longitudinal polarization \( \delta P_L(k,t) \) is defined by the expression
\[ \delta P_L(k,t) = \mu \int dr e^{-ikr} \int d\omega \left[ \hat{e}\hat{\alpha}(\omega) \delta p(r,\omega,t) \right] \] (7)
where \( \hat{\alpha} \) is a unit vector with orientation \( \omega \) and \( \mu \) is the magnitude of the dipole moment of a solvent molecule. It has been shown elsewhere that, in a linear theory, the decay of the polarization time correlation function is exponential:
\[ \delta P_L(-k) \delta P_L(k) \delta P_L(k,t) = \frac{N_{\mu^2}}{3} \left[ 1 + \rho_0 \left( h_k(k) + 2h_0(k) \right) \right] \] (8)
where \( N \) is the total number of solvent molecules and \( h_k(k) \) and \( h_0(k) \) are the usual anisotropic parts of the two-particle pair correlation function. \( h_k(k) \) and \( h_0(k) \) are related to \( C_g(k) \) and \( C_p(k) \) by the Ornstein–Zernike relation. Since the bare field of an ion or of a dipole is known, it is now straightforward to write analytic expressions of the reaction coordinate time correlation function, \( \Delta G^\#(t) \), for both the models. The explicit expression of \( \Delta G^\#(t) \) for model II is given by
\[ \Delta G^\#(t) = X(t) / X(0) \] (11a)
with
\[ X(t) = \int_0^\infty dq \left( (\delta P_L(-q) \delta P_L(q)) e^{i\omega q(t)} \right) \left[ \frac{8}{(R + 1)^2} + \frac{2}{2} \right] \] (11b)
where \( f(z) \) is the spherical Bessel function of order unity and

---

adiabatic electron-transfer reaction (for model I given by eq 1.368 and I.370) respectively, where the rotational diffusion coefficient of the solvent. The values of the dielectric constant and the reduced density of the solvent are 18.0 and 0.8, respectively. The values of the longitudinal relaxation time (\( t_L \)) and the Debye relaxation time (\( t_D \)) are 0.076\( D_h^{-1} \) and 1.368\( D_h^{-1} \), respectively, where \( D_h \) is the rotational diffusion coefficient of the solvent. \( \beta e^2/\sigma = 140.0 \).

Numerical Results

We now present numerical results of our calculations of the effective barrier-crossing frequency, \( \nu \), defined by the relation

\[
\nu = k \exp[-\beta \Delta G^\#]
\]

(12) The explicit expression of \( \nu \) can be obtained from eqs 4–11. In our formalism, the free energy of activation, \( \Delta G^\# \), for model I is given by the expression

\[
\Delta G^\# = \frac{e^2}{4\pi\sigma} \int_0^\infty dq \left[ 1 - \frac{1}{\epsilon(q)} \right] \int_{(v/2)(R+1)}^{\infty} dx \frac{\sin x}{x} \]

(13) where \( q = k \alpha \). The above expression correctly reduces to the corresponding dielectric continuum formula for the intrinsic barrier(16) when \( \epsilon(k) \) is approximated by \( \epsilon_0 \) and when \( R \) is very large. We have discussed elsewhere(17) that the replacement of \( \epsilon(k) \) by \( \epsilon_0 \) can be a poor approximation when the reactant–solvent size ratio is small (\( R < 1 \)). For model II, the expression of the barrier height is given by the expression for the solvation energy of a dipole. In the numerical calculations, we have considered both the weakly adiabatic and the strongly adiabatic cases. In the former case, we have taken \( \epsilon_0 = 4\omega_0 \) and for the strongly adiabatic case, we have taken \( \epsilon_0 = \omega_0 \). We have calculated the frequency-dependent friction, \( g_f(x) \), by using the generalized Langevin equation for the motion of the reaction coordinate in the overdamped limit, thus ignoring the acceleration term. In all our numerical calculations we have used the mean-spherical approximation (MSA) for the two-particle direct correlation function. This is fairly accurate at low dielectric constant.

Figures 1 and 2 show the results of our calculations of \( \nu \) for model I. In Figure 1, the dependence of \( \nu \) on the translational parameter, \( p' \), in the weakly adiabatic limit (\( \omega_0 = 4\omega_0 \)) is shown. It is seen that the rate of electron transfer increases with an increase in the value of \( p' \). The increase in the electron-transfer rate is higher for smaller solute size. This is because when the size of the reactant is small, the reaction probes more of the intermediate wavevector processes than when it is large. The relaxation of the solvent polarization at intermediate wavevectors becomes increasingly faster as the value of the translational parameter, \( p' \), is increased. This large effect of the translational modes on the intermediate-wavelength processes comes from two sources. First, small spatial displacements, which have a pronounced effect at these length scales, are quite fast (because rate varies as \( D_f p'^2 \)). Second, because of strong intermolecular correlations between nearest neighbors, orientational relaxation is rather slow.

In Figure 1, we have also plotted the prediction of the continuum model (which includes only the \( k = 0 \) mode contribution toward the solvent polarization relaxation) for the rate, given by \( \nu = (2\pi\tau_p)^{-1} \), by a dashed line. The calculated rate is less than the continuum model prediction for \( p' = 0 \) but becomes greater as \( p' \) is increased.

Figure 2 shows the dependence of \( \nu \) on translation but in the strongly adiabatic limit (\( \omega_0 = \omega_0 \)). In this limit the electron transfer occurs at a lower rate than that in the weakly adiabatic case and also the dependence on \( p' \) is somewhat weaker. The reason is that, in the weakly adiabatic limit, the reaction probes the high-frequency components of the solvent response. At large \( p' \), translational modes populate these high-frequency components, so the dependence on \( p' \) is stronger for a weakly adiabatic reaction.

(16) The dielectric continuum formula for the intrinsic barrier involving an isolated redox couple is \( \Delta G^\# = (e^2/8\sigma)(1 - \epsilon_0^2) \) in a liquid of nonpolarizable molecules.
Electron Impact Mass Spectrometry of Cholesterol in Supersonic Molecular Beams

Aviv Amirav

Sackler Faculty of Exact Sciences, School of Chemistry, Tel-Aviv University, Ramat Aviv 69978, Israel
(Received: March 1, 1990)

The effect of vibrational supercooling on the electron impact mass spectrometry of cholesterol was studied in supersonic molecular beams. An extensive mass spectral simplification was observed at 20 eV electron energy. The parent undissociated molecular ion becomes the dominant peak even at 70 eV electron energy but the conventional complex fragmentation pattern is retained in spite of the large vibrational cooling. Some of the unique aspects of electron impact mass spectrometry in supersonic molecular beams are mentioned.

Since the pioneering demonstration of Smalley et al., supersonic molecular beams (SMB) revolutionized the research of optical spectroscopy and intramolecular dynamics. The extreme molecular vibrational-rotational cooling considerably simplifies laser-induced fluorescence spectra of large polyatomic molecules, eliminates sequence congestion, and provides clear information on the initial and final ro-vibronic quantum states. On the other hand, vibrational temperature effects on electron impact induced ion fragmentation are well-known and documented in electron impact mass spectrometry of cholesterol in supersonic molecular beams. The dramatic effect of the translational diffusion on the rate of an electron-transfer reaction has a simple physical origin. At small length scales, the collective orientational relaxation of a dense dipolar liquid is slow in the absence of translational contribution. However, the translational modes are especially effective at small length scales. These two effects combine to give rise to the marked dependence of the rate constant on p' that enters through o_R. This explains the weak p'dependence of the ratio k^{GH}/k^{ST}.

Acknowledgment. This work was supported in part by NSF, USA (G.R.F.), CSIR, INDIA (A.C.), and INSF, INDIA (B.B.). B.B. is a Homi Bhabha Fellow for 1989-1991.

---